

TITLE: CHEMICAL KINETICS IN THE COMA

**MASTER**

AUTHOR(S): Walter F. Huebner

SUBMITTED TO: College Park Colloquia on Chemical Evolution  
Colloquium V  
Comets and the Origin of Life  
October 29-31, 1980

DISCLAIMER

By acceptance of this article, the publisher recognizes that the U.S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or to allow others to do so, for U.S. Government purposes.

The Los Alamos Scientific Laboratory requests that the publisher identify this article as work performed under the auspices of the U.S. Department of Energy.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

University of California



**LOS ALAMOS SCIENTIFIC LABORATORY**

Post Office Box 1663 Los Alamos, New Mexico 87545  
An Affirmative Action/Equal Opportunity Employer

**CHEMICAL KINETICS IN THE COMA\***

**by**

**W. F. Huebner**

**Theoretical Division (T-4/T-6)**

**Los Alamos Scientific Laboratory**

**Los Alamos, New Mexico 87545**

---

**\*Work performed under the auspices of the U. S. Department of Energy  
and supported by the National Aeronautics Space Administration,  
Planetary Atmospheres Program.**

## ABSTRACT

Physical and chemical conditions in the coma of a bright "new" comet are related to the composition of the nucleus. Chemical and photolytic processes are described and related to distance in the coma above the nucleus and to heliocentric distance of the comet. Comparison of the model with coma observations leads to some restrictions about the nucleus composition. It is expected that these restrictions become more stringent as coma models are developed further and as observations become more detailed.

## I. INTRODUCTION

After the sun grazing comet Ikeya Seki (1965 VIII) had moved through the sun's corona, its activity had been reduced only slightly. Yet a comet nucleus is so small--less than several tens of kilometers--that it cannot be resolved with big telescopes. This is a beautiful demonstration that the source of cometary activity, the nucleus, must be compact and must have enough mass to survive a close encounter with the sun. Ikeya Seki split and comet West (1976 VI) broke into four pieces; this indicates that the nucleus lacks dynamical strength--it probably consists of loosely compacted frozen gases and dust. These conditions are consistent with Whipple's icy conglomerate model of the nucleus (Whipple, 1950; 1951). No direct evidence and little more indirect evidence exists about the physical structure and chemical composition of the nucleus.

Since we cannot observe the nucleus directly--this will have to await a mission to a comet--we must concentrate our attention on the next larger feature that is observable: the coma. It is up to  $10^5$  km in size in visible light and up to  $10^7$  km in the ultraviolet (the hydrogen coma in Lyman alpha). It is our plan to model the coma physically and chemically--starting with some assumptions about the nucleus--compare the model results with observations and deduce from them the conditions of the nucleus.

The observed species of the coma are shown in Table I. It shows that the frozen volatiles in the nucleus contain H, C, N, O, and S. But not even the relative abundances of these are well known. The ion and dust tails are extensions of the coma caused by solar wind interaction with the cometary ions and by radiation pressure on dust. Comet tails are therefore not as useful for our purposes as the coma.

Earlier it was thought that comets originated in the solar system, beyond Jupiter. Under such conditions the composition of the nucleus should be in chemical equilibrium or close to it:  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{NH}_3$ , and possibly  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{C}_2\text{N}_2$  etc. (see, e.g., Wurm, 1943). Now it is believed that comets have their origin in the presolar nebula or a companion fragment thereof (see, e.g., Biermann and Michel, 1978).

One therefore expects that molecules that have been detected in dense interstellar clouds will also be present. Furthermore, ultraviolet radiation and cosmic rays may have converted some of these molecules to nonvolatile, heavy organic materials. Even if the relative abundance of H, C, N, O, and S is cosmic, during comet formation some of these atoms will be bound in grains, others in the nonvolatile organic compounds and still others in extremely volatile compounds that never condensed. We therefore do not know the relative abundance available in the volatile fraction of the frozen gases in the nucleus. Much less do we know what the relative composition of these molecules is. We are at the limit of our knowledge. There are too many unknowns, therefore our model is idealized:

- The nucleus may have a very odd shape--we assume a spherical shape.
- The nucleus may be highly heterogeneous; spotty on the surface, pockets of volatiles under the surface--we assume a homogeneous nucleus.
- The nucleus is composed of dust and volatile and nonvolatile organics--we consider only the volatile material.
- Radiation pressure and solar wind distort the coma--we assume the coma is spherical.
- Attenuation of solar radiation in the coma depends on the angle of incidence--we assume that incidence is at a right angle.
- Outgassing will be nonuniform--we assume it is uniform and spherically symmetric.

Despite of the many simplifications, we still have a complex problem to solve. The model described below is based on the work by Giguere and Huebner, 1978a and Huebner and Giguere, 1980.

## II. PHYSICS

Solar radiation incident on the comet nucleus is in part absorbed, the rest is reflected. The larger the albedo, the larger the reflection. Part of the absorbed energy is reradiated in the infrared, the balance changes the frozen gases from the solid phase to a vapor (sublimation from solid to gas). At large heliocentric

distance most of the absorbed energy is reradiated in the infrared; at small heliocentric distance the equilibrium temperature is sufficiently high so that most of the energy goes into sublimation of the surface materials. The relationship is nonlinear.

From energy balance and the equation of state, which consists of the Clausius--Clapeyron equation coupled to the ideal gas equation, we calculate the equilibrium surface temperature  $T$ , gas pressure, gas density  $n_0$ , gas production rate per unit surface area  $Z$  and sound speed  $v_s$ . The quantities are calculated with assumed parameters for the albedo  $A$  and the emissivity  $\epsilon$ . The mean latent heat  $L$ , which also enters as a parameter, is determined from the assumed composition of the frozen gases. From this composition are also determined the mean molecular weight  $M$  and the adiabatic exponent  $\gamma$  (ratio of specific heats). Typical values are  $A = 0.3$ ,  $\epsilon = 0.7$ ,  $L \cong 8$  kcal/mol,  $\gamma \cong 1.35$ ,  $M \cong 22$  and for a nucleus of 1 km radius at a heliocentric distance of 1 AU  $T \cong 150^\circ\text{K}$ ,  $Z \cong 3 \times 10^{17}$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ,  $n_0 \cong 4.5 \times 10^{13}$  molecules/ $\text{cm}^3$  and  $v_s \cong 0.3$  km/s. The initial outstream velocity is  $v_s/4$ .

Applying the usual conservation laws of energy, momentum, and mass we calculate the fluid dynamics of isotropic outflow. Using the adiabatic exponent as the polytropic exponent, the fluid flow obeys the von Mises solution of supersonic flow. The asymptotic value of the supersonic outflow velocity, typically 0.7 km/s, is attained at several tens to a hundred nuclear radii above the surface. It is important to note that because of mass conservation, the gas density varies as

$$n_{i+1} = n_i (v_i/v_{i+1})(r_i/r_{i+1})^2.$$

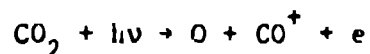
This deviates markedly from a  $r^{-2}$  variation near the nucleus.

From the density-distance relationship, the photo cross sections of the coma gas constituents and their relative abundances, we can calculate the attenuation of the solar ultraviolet radiation. This is done wavelength dependent, averaged over wavelength bins a few to 50 Å wide. Cross-section data are available for most of the important

mother molecules in the coma. The attenuation depends not only on the distance above the nucleus, but also on the angle of incidence of the sun light. However, preliminary calculations indicate that the attenuation does not vary strongly with angle as measured from the comet-sun axis except for a narrow segment in the antisolar direction (Giguere and Huebner, 1978b). The amount of solar uv radiation is important for determining dissociation and ionization which initiate chemical reactions in the inner coma.

### III. CHEMISTRY

Reaction processes that we find to be important for initiating and maintaining chemical reactions are summarized in Table II. The least important of these processes are listed near the bottom. Nearly 100 photolytic processes are included in our model calculation; many are considered in great detail, others for which cross sections are not available are estimated. Photodissociative ionization (PDI) is an important process in the inner coma. PDI is a process in which a photon causes a molecule to be ionized into an excited state; the excited state of the molecular ion then decays by dissociation. The process



is very important for the production of  $\text{CO}^+$  deep in the coma where it is observed. PDI of other CO-bearing molecules gives similar results. Photon energy in excess of threshold for ionization produces hot electrons. These have enough energy to produce more ionization and dissociation by impact. Similarly, solar wind electrons can produce ions and radicals at the contact surface in the coma. These impact processes have not yet been included in our model. About 500 chemical reactions are available in the program and are used in accordance with the assumed initial chemical composition. Over 100 different chemical species react with each other. There is a differential equation for each species coupling

it to other species. Since some reactions proceed very fast and others slowly or not at all until the reactants have been built up from other reactions, it is important to use a stiff differential equation solver technique.

There are two features which distinguish our chemistry from that used to model interstellar clouds: (1) Inner coma temperatures are typically 150°K which is much warmer than the temperatures in interstellar clouds and much closer to the laboratory conditions at which rate constants are being measured. (2) Our calculations are time dependent chemical kinetics, while a steady state is assumed for interstellar clouds.

#### IV. COMBINING PHYSICS AND CHEMISTRY

Our model calculations are based on the processes occurring in a thin shell of coma gases as it expands and moves outward. Therefore, chemical reactions take place in a continually diluting gas exposed to a continually increasing solar ultraviolet radiation flux. The practical details are illustrated in Fig. 1. The time step for the chemical reactions is much smaller than the fluid dynamic time step at which the density and attenuated solar flux are recalculated. Fluid dynamic time steps are approximately logarithmic. Only at large distances from the nucleus does the chemical time step approach the fluid dynamic time step. It is important to recognize that in this procedure chemical steady state may not be reached, the dilution of the gas may "freeze-in" some species that otherwise might have reacted further.

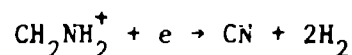
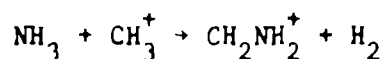
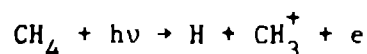
#### V. RESULTS

Considering the origin of life, biological molecules of ever increasing complexity must have been synthesized by chemical reactions from simple molecules and radicals under nonequilibrium conditions. A similar sequence of events also occurs in comet comae. Solar uv radiation dissociates and ionizes molecules producing highly reactive species that combine in new ways, forming more complex species. But solar uv is relentlessly dissociating and ionizing; what it created in

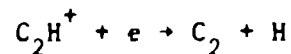
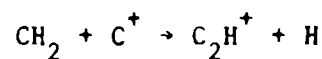
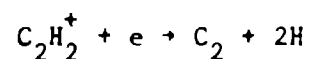
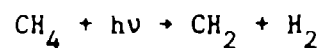
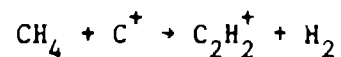
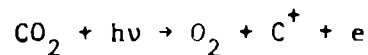
the inner coma it destroys again in the outer coma. For a comet near the sun, most molecules in the coma will be dissociated into atoms and eventually even these will be ionized.

Starting with a nuclear mixture that in the gas phase is nearly in chemical equilibrium ( $H_2O$ ,  $CH_4$ ,  $NH_3$  with some  $CO_2$  or  $CO$  added) our model fails to produce the observed quantities of  $C_3$  and  $C_2$ . CN production is marginally in agreement with observations at 1 AU heliocentric distance but is underproduced at larger distances from the sun. (Of the neutral species, CN has the largest extent in the visible coma of most comets and is the first species detectable when such a comet approaches the sun).

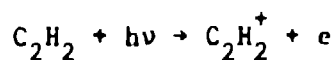
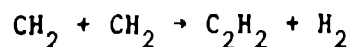
The main production mechanism from  $CH_4$  and  $NH_3$  is



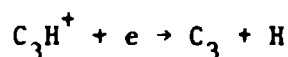
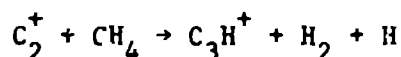
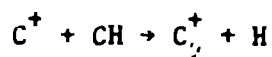
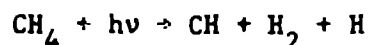
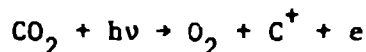
$C_2$  is produced primarily from  $CH_4$  and  $CO_2$ :



A competing process for the production of  $C_2H_2^+$  in the reaction chain on the left comes from the chain on the right



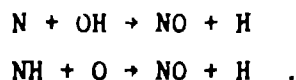
$\text{CH}_4$  and  $\text{CO}_2$  also produce  $\text{C}_3$ :



If, on the other hand, comets are formed in the presolar nebula or a companion fragment of that nebula, then the frozen gases in a comet nucleus may also contain molecules that have been detected in interstellar space. With the constraint that the abundance ratio of C:N:O is cosmic and the ratio of H:O  $\cong$  2 (a typical value deduced from observations in comets), we have assumed a mixture which contains about 90%  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{CO}$ ,  $\text{CH}_4$ , and  $\text{CO}_2$ , a few percent of  $\text{N}_2$  and CO and trace amounts of HCN,  $\text{CH}_3\text{CN}$ ,  $\text{CH}_3\text{NH}_2$ ,  $\text{H}_2\text{C}_3\text{H}_2$ ,  $\text{C}_2\text{H}_2$ , and  $\text{NH}_3$ . The first two trace molecules (0.9% of the total mixture) are the main source for CN. Allene,  $\text{H}_2\text{C}_3\text{H}_2$ , (0.2% of the mixture) is the source for  $\text{C}_3$ . This and acetylene (0.1%) are the main source for  $\text{C}_2$ . Model calculations have been made for a nucleus of 2.5 km radius at heliocentric distances of 0.59, 1.0, and 3.0 AU. Details of the calculations will be reported at a later time by Biermann et al. (1981). Some column densities for the three heliocentric distances are shown in Fig. 2. Consistent with observations of bright "new" comets, CN is dominant and closely followed by  $\text{C}_3$  at various distances from the sun. It should be noted that the CN and  $\text{C}_3$  column densities fall off with distance from the nucleus while the profile for  $\text{C}_2$  remains constant to a distance beyond  $10^4$  km. Observed column densities are average values to distances of  $10^4$  or several times  $10^4$  km. Because of the profile, the average column densities for CN and  $\text{C}_3$  from our model are much closer to the average value of  $\text{C}_2$  than appears from Fig. 2. Some comparisons with observations made by A'Hearn and coworkers (A'Hearn, 1975; 1980; A'Hearn et al., 1980) of average column densities are summarized in Table III.

Both, the near chemical equilibrium compositions and the interstellar composition give the ratio of  $\text{CO}^+:\text{H}_2\text{O}^+$  column density close to or less than one. This is contrary to the only value that is based on observations--obtained from comet Kohoutek--which indicates the ratio is about 10. The reason why our model gives a ratio so much smaller than observations is not known.  $\text{CO}^+$  has a large rate coefficient for charge exchange; a collision with a neutral species changes  $\text{CO}^+$  to  $\text{CO}$ . If more of the hydrogen and oxygen were tied up in CO-bearing molecules like  $\text{H}_2\text{CO}$ ,  $\text{HCOOH}$ , etc., rather than in  $\text{H}_2\text{O}$ , then the  $\text{CO}^+:\text{H}_2\text{O}^+$  ratio would be improved. Another possibility is that water is in the form of frozen grains in the inner coma, i.e., less water is in its gas phase and therefore not available for charge exchange. When the ice grains vaporize at a larger distance from the nucleus, the molecular density is low and charge exchange is less effective. New observational determinations of the ratio are also very desirable.

Some species that are not direct dissociation products in our assumed composition but are predicted with reasonable abundance by our model and have not been observed yet include  $\text{NO}$ ,  $\text{HCO}^+$ ,  $\text{H}_3\text{O}^+$  and  $\text{HCO}_2^+$ .  $\text{NO}$  is produced by the following two reactions at various distances in the coma



The production mechanisms for the other three molecules stem from various reactions. Tables IV, V, and VI summarize where in the coma the three most important reactions for each of the three species dominates. These three tables also serve to illustrate that it is not possible to greatly simplify the chemical reaction network. A reaction important in one part of the coma may be completely subordinate to another reaction producing the same species in another part of the coma or at another heliocentric distance of the comet.

Having included many new species in the initial composition which produce observed species by direct dissociation raises the question of how important chemistry is. A check calculation was made with the chemistry (except photolytic processes) turned off. Table VII shows that chemistry still plays an important role for many species.

## VI. CONCLUSIONS

Whereas it was not possible with the present model to match the observed column densities for  $C_2$  and  $C_3$  and only marginally for CN in the case of a starting mixture near chemical equilibrium, there is no difficulty when some interstellar molecules containing the  $C_2^-$ ,  $C_3^-$  and  $CN^-$  groups are included in the mixture of frozen gases. Although it appears likely, there is no proof that comets contain interstellar molecules. Species composed of the same atomic constituents (H, C, N and O) must be expected to have similar products from decay and chemistry. Therefore, similarity of cometary and interstellar molecules may be coincidental. The fact that only traces of some interstellar molecules produce the observed abundances of  $C_2$ ,  $C_3$  and CN places a severe restriction on the nucleus composition.

The abundance of some ions, in particular the abundance ratio  $CO^+ : H_2O^+$  is still not fully understood. More physical processes need to be included in the model and more observational data are needed.

# REFERENCES

1. A'Hearn, M. F. 1975 Astron. J. 80, 861.
2. A'Hearn, M. F. and coworkers 1980, private communication.
3. A'Hearn, M. F., Hanisch, R. J. and Thurber, C. H. 1980, Astron. J. 85, 74.
4. Biermann, L. and Michel, K. W. 1978, Moon Planets 18, 447.
5. Biermann, L., Giguere, P. T. and Huebner, W. F. 1981, in preparation.
6. Giguere, P. T. and Huebner, W. F. 1978a, Astrophys. J. 223, 638.
7. Giguere, P. T. and Huebner, W. F. 1978b, Bull. A. A. S. 10, 614.
8. Huebner, W. F. and Giguere, P. T. 1980, Astrophys. J. 238, 753.
9. Sivaraman, K. R., Babu, G. S. D., Bappu, M. K. V. and Parthasarathy, M. 1979, Mon. Not. r. Astr. Soc. 189, 897.
10. Whipple, F. L. 1950, Astrophys. J. 111, 375.
11. Whipple, F. L. 1951, Astrophys. J. 113, 464.
12. Wurm, K. 1943, "Die Natur der Kometen" Mitt. Hamb. Sternw. 8, No. 51.

TABLE I

## OBSERVED CONSTITUENTS

Head: H, C, O, S

CH, NH, OH, C<sub>2</sub>, CN, CO, CS

PH<sub>2</sub>, H<sub>2</sub>O, HCN, C<sub>3</sub>

CH<sub>3</sub>CN

Sun Near: Na

Sun Grazer: Si, Ca, K, V, Cr, Mn, Fe, Co, Ni, Cu

Dust: Silicates

Tail: C<sup>+</sup>

CH<sup>+</sup>, OH<sup>+</sup>, CO<sup>+</sup>, CN<sup>+</sup>, N<sub>2</sub><sup>+</sup>

H<sub>2</sub>O<sup>+</sup>, CO<sub>2</sub><sup>+</sup>

Sun Grazer: Ca<sup>+</sup>

TABLE II  
CHEMICAL REACTION PROCESSES [WITH EXAMPLES]

Photodissociation [ $h\nu + \text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$ ]  
 Photoionization [ $h\nu + \text{CO} \rightarrow \text{CO}^+ + e$ ]  
 Photodissociative Ionization [ $h\nu + \text{CO}_2 \rightarrow \text{O} + \text{CO}^+ + e$ ]  
 Electron Impact Dissociation [ $e + \text{N}_2 \rightarrow \text{N} + \text{N}$ ]  
 Electron Impact Ionization [ $e + \text{CO} \rightarrow \text{CO}^+ + 2e$ ]  
 Electron Impact Dissociative Ionization [ $e + \text{CO}_2 \rightarrow \text{O} + \text{CO}^+ + 2e$ ]  
 Positive Ion-Atom Interchange [ $\text{CO}^+ + \text{H}_2\text{O} \rightarrow \text{HCO}^+ + \text{OH}$ ]  
 Positive Ion Charge Transfer [ $\text{CO}^+ + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}^+ + \text{CO}$ ]  
 Electron Dissociative Recombination [ $\text{C}_2\text{H}^+ + e \rightarrow \text{C}_2 + \text{H}$ ]  
 3-Body Positive Ion-Neutral Association [ $\text{C}_2\text{H}_2^+ + \text{H}_2 + \text{M} \rightarrow \text{C}_2\text{H}_4^+ + \text{M}$ ]  
 Neutral Rearrangement [ $\text{N} + \text{CH} \rightarrow \text{CN} + \text{H}$ ]  
 3-Body Neutral Recombination [ $\text{C}_2\text{H}_2 + \text{H} + \text{M} \rightarrow \text{C}_2\text{H}_3 + \text{M}$ ]  
 Radiative Electronic State Deexcitation [ $\text{O}(^1\text{D}) \rightarrow \text{O}(^3\text{P}) + h\nu$ ]  
 Electron Impact Electronic State Quenching [ $e + \text{O}(^1\text{D}) \rightarrow e + \text{O}(^3\text{P})$ ]  
 Radiative Recombination [ $e + \text{H}^+ \rightarrow \text{H} + h\nu$ ]  
 Radiation Stabilized Positive Ion-Neutral Association [ $\text{C}^+ + \text{H} \rightarrow \text{CH}^+ + h\nu$ ]  
 Radiation Stabilized Neutral Recombination [ $\text{C} + \text{C} \rightarrow \text{C}_2 + h\nu$ ]  
 Neutral-Neutral Associative Ionization [ $\text{CH} + \text{O} \rightarrow \text{HCO}^+ + e$ ]

TABLE III

SOME COMPARISONS OF OBSERVED AND MODEL CALCULATED COLUMN DENSITIES

Species	Comet	Heliocentric Distance [AU]	Distance into Coma [ $10^4$ km]	Log Column Density [ $\text{cm}^{-2}$ ]	
				Observed (from A'Hearn)	Interstellar Composition
CN	West	0.6	5	12.3	12.7
		1.0	5	11.8	12.3
C <sub>2</sub>	West	0.6	5	12.3	12.3
		0.6	1	13.6*	12.6
		1.0	5	12.2	11.6
	Kohoutek	1.0	3	11.5	11.6
C <sub>3</sub>	West	0.6	5	12.0	12.0
		1.0	5	12.2	11.7
NH <sub>2</sub>	Kohoutek	1.0	3	10.8	10.7
CH	Kohoutek	0.6 <sup>pre</sup>	5	11.5	10.7

\*Sivaraman et al., 1979

<sup>pre</sup>post perihelion

TABLE IV  
PRODUCTION PATHS FOR  $\text{HCO}^+$

	Distance into Coma R [km]			
	$1 \times 10^3$	$1 \times 10^4$	$3 \times 10^4$	$1 \times 10^5$
$\text{H}_2\text{CO} + h\nu \rightarrow \text{H} + \text{HCO}^+ + e$	1			
$\text{CO}^+ + \text{H}_2\text{O} \rightarrow \text{HCO}^+ + \text{OH}$	2	1	4	
$\text{CH}_3^+ + \text{H}_2\text{CO} \rightarrow \text{HCO}^+ + \text{CH}_4$	3			
$\text{H}_2\text{O}^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{OH}$	4	3		
$\text{CO}^+ + \text{H}_2 \rightarrow \text{HCO}^+ + \text{H}$		2	1	2
$\text{C}^+ + \text{H}_2\text{O} \rightarrow \text{HCO}^+ + \text{H}$		4	2	4
$\text{N}^+ + \text{CO}_2 \rightarrow \text{HCO}^+ + \text{O}$			3	1
$\text{H}_2^+ + \text{CO} \rightarrow \text{HCO}^+ + \text{H}$				3

TABLE V  
PRODUCTION OF  $\text{H}_3\text{O}^+$

	0.59 AU				1.0 AU				3.0 AU			
	A	B	C	D	A	B	C	D	A	B	C	D
$\text{H}_2\text{O}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{OH}$	1	1	3		1	1	1		1	1	1	1
$\text{HCO}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CO}$	2	2	1		3	3	3		3			
$\text{CH}_4^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3$	3	3				2	2			2	2	2
$\text{H}_2\text{O}^+ + \text{H}_2 \rightarrow \text{H}_3\text{O}^+ + \text{H}$				2	1				2			
$\text{OH}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{O}$				2				3				
$\text{H}_2^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{H}$				3				1				
$\text{H}_2\text{CO}^+ + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HCO}$					2				2	3	3	
$\text{H}_2\text{O}^+ + \text{CH}_4 \rightarrow \text{H}_3\text{O}^+ + \text{CH}_3$												3

DISTANCE INTO COME--A... $1 \times 10^3$  km, B... $1 \times 10^4$  km, C... $3 \times 10^4$  km, D... $1 \times 10^5$  km

TABLE VI  
PRODUCTION OF  $\text{HCO}_2^+$

	Distance Into Coma R [km]			
	$1 \times 10^3$	$1 \times 10^4$	$3 \times 10^4$	$1 \times 10^5$
$\text{CO}_2^+ + \text{H}_2\text{O} \rightarrow \text{HCO}_2^+ + \text{OH}$	1	2	2	
$\text{CO}_2^+ + \text{H}_2 \rightarrow \text{HCO}_2^+ + \text{H}$	2	1	1	1
$\text{CH}_4^+ + \text{CO}_2 \rightarrow \text{HCO}_2^+ + \text{CH}_3$	3	3	3	
$\text{HCO}^+ + \text{OH} \rightarrow \text{HCO}_2^+ + \text{H}$				3
$\text{OH}^+ + \text{CO}_2 \rightarrow \text{HCO}_2^+ + \text{O}$				2

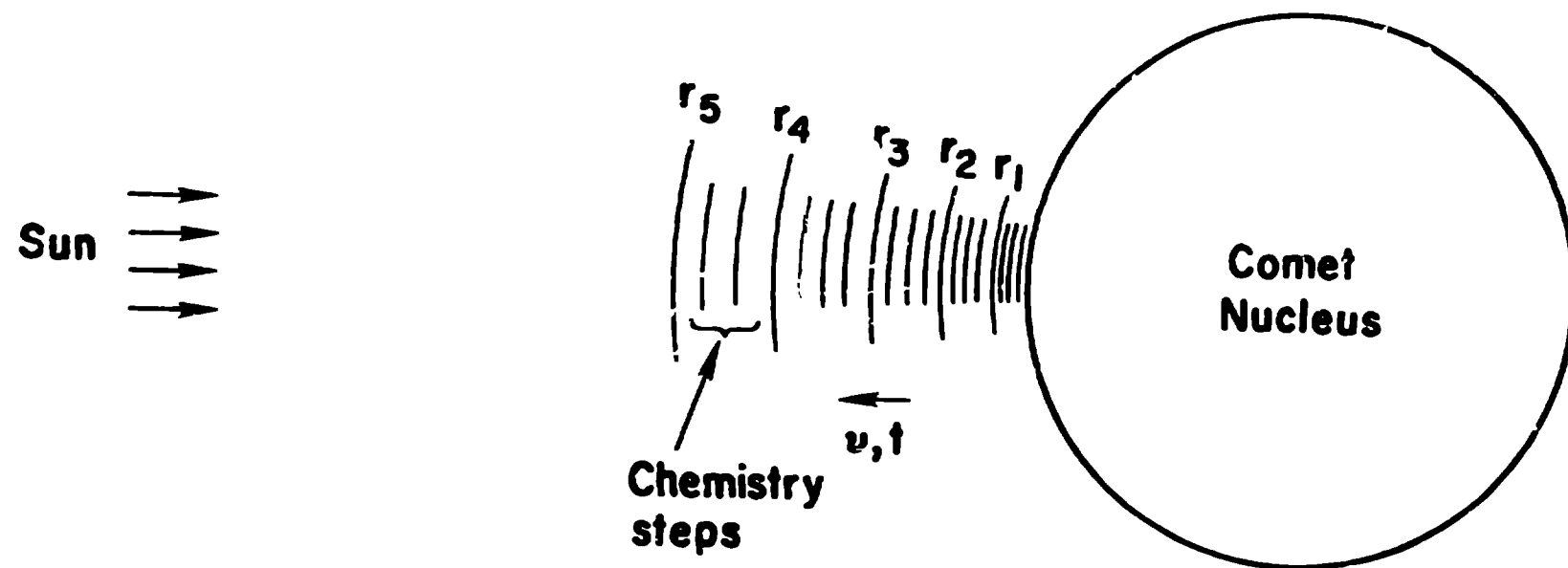
TABLE VII  
 RATIO OF COLUMN DENSITY AT  $10^4 \text{ km}$ : WITH CHEM/WITHOUT CHEM

	HELIOCENTRIC DISTANCE		
	0.59 AU	1.0 AU	3.0 AU
O( $^1\text{D}$ )	$4.1 \times 10^{-3}$	$4.0 \times 10^{-3}$	$2.3 \times 10^{-3}$
O	1.6	1.8	2.9
C( $^1\text{D}$ )	.32	.25	$7.8 \times 10^{-2}$
C	1.1	1.2	1.0
C $^+$	1.0	.93	.91
CO $^+$	$3.0 \times 10^{-2}$	.12	.76
CO $_2^+$	$3.3 \times 10^{-2}$	.12	.75
H $_2$ O $^+$	$3.6 \times 10^{-2}$	.11	.74
N $_2^+$	$3.2 \times 10^{-2}$	.13	.77
C $_2$	1.4	1.1	1.03
NO	$\infty$	$\infty$	$\infty$
HCO $_2^+$	$\infty$	$\infty$	$\infty$
H $_3$ O $^+$	$\infty$	$\infty$	$\infty$

## FIGURE HEADINGS

Fig. 1. Combining physics and chemistry. Time steps for chemical kinetics are small. Time steps for fluid dynamics are larger ( $r_1, r_2, \dots \sim$  logarithmically spaced). Many species do not reach chemical steady state in a fluid dynamic step. Opacity is calculated at each fluid dynamic step as a function of wavelength.

Fig. 2. Column density  $N$  versus distance  $\rho$  from the center of the nucleus into the coma for some species as predicted by our model calculations, assuming an interstellar composition. Radius of nucleus is 2.5 km. A--at heliocentric distance  $r = 0.59$  AU, which corresponds to perihelion distance of Halley's comet. B--at  $r_h = 1.0$  AU. C--at  $r_h = 3.0$  AU.



*Fig. 1*

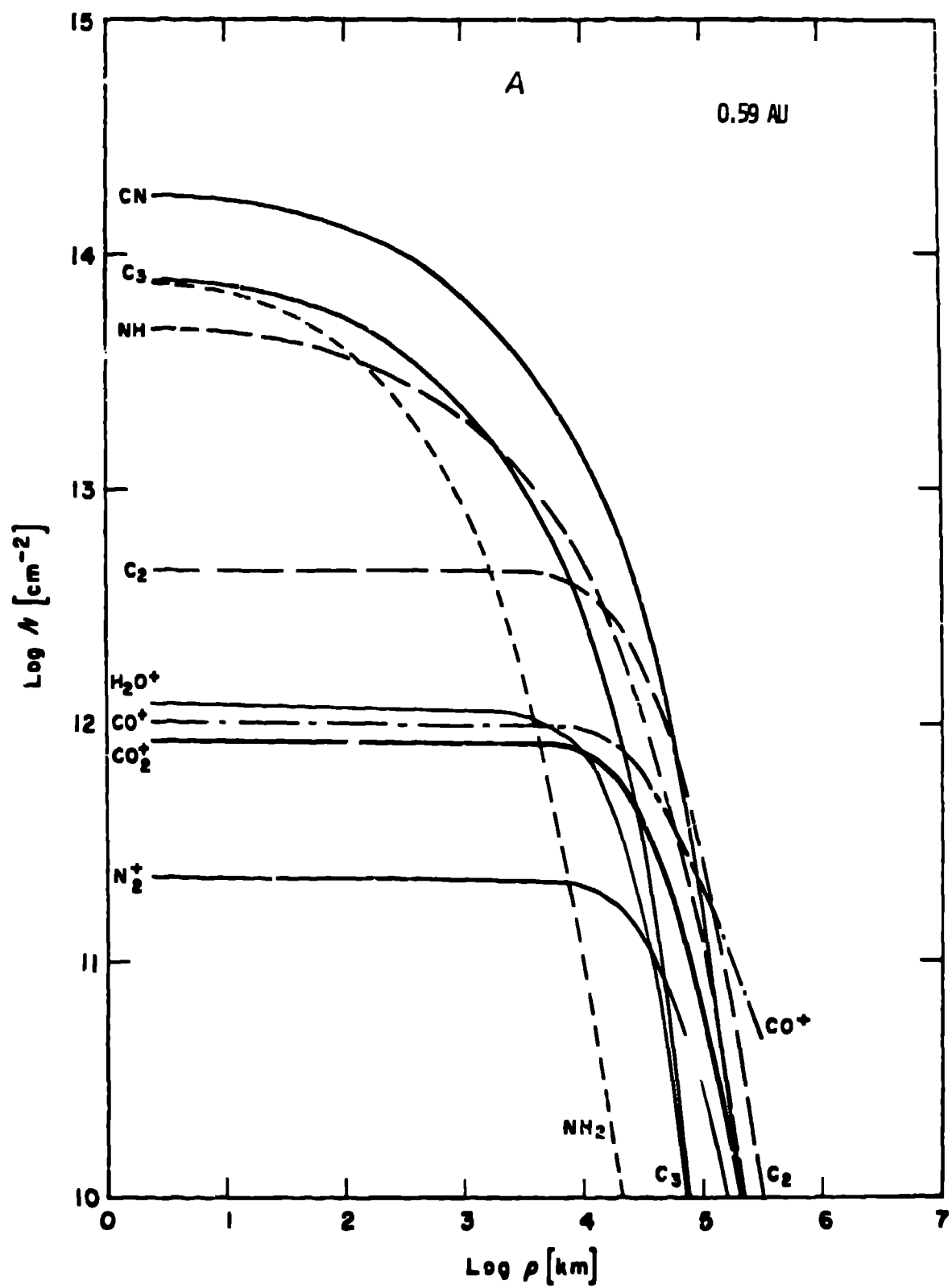


Fig. 2

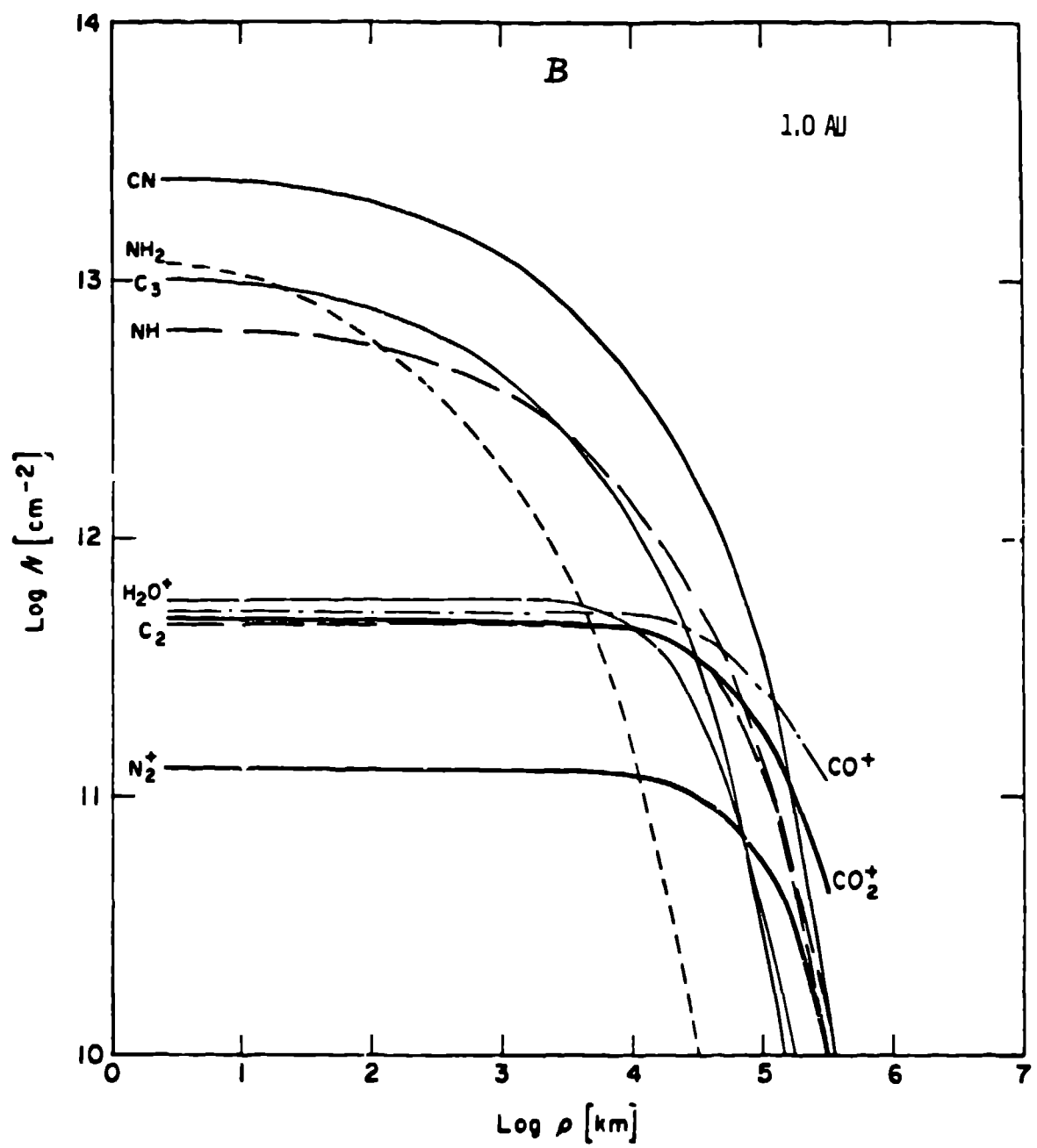


Fig. 2

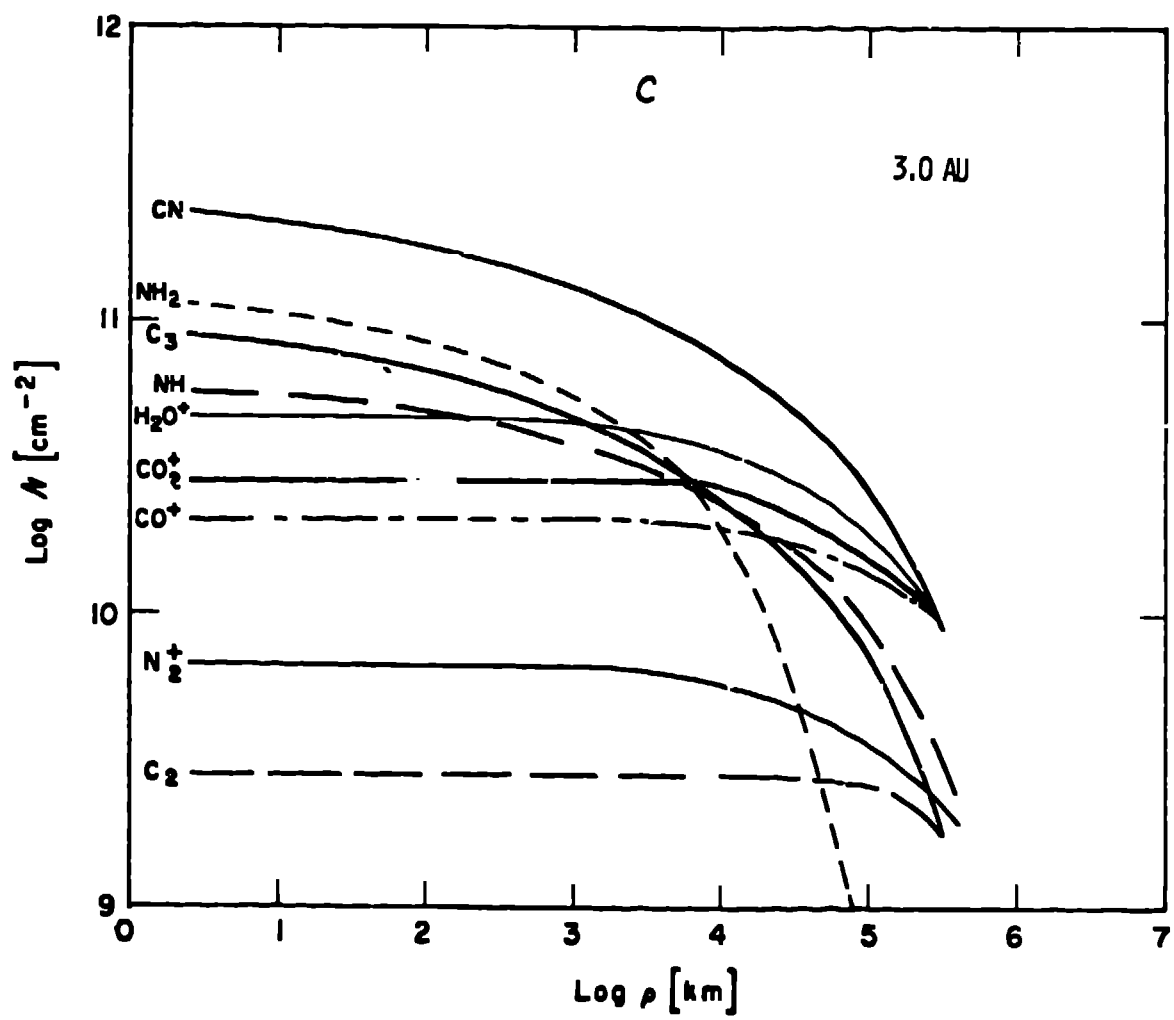


Fig. 2